

**MAXIMIZING THE EFFICACY OF
THIOCYANATE SCAVENGERS IN OILFIELD BRINES**

BACKGROUND

[0001] In recent times there has been considerable discussion in the oilfield technical literature suggesting that in oilfield brines the commonly-used inorganic thiocyanate brine corrosion inhibitors tend to decompose to hydrogen sulfide, alkyl sulfides, disulfides, and mercaptans. This can lead during downholes operations to sulfide stress corrosion cracking ("SSCC") of corrosion resistant alloys in piping, casings, tubings, *etc.* that are present in downhole wells, these components being commonly referred to by those in the art as "OCTG" which stands for "oil country tubular goods". The severity of the problem has led at least one author in the field to suggest that inorganic thiocyanates should be avoided in brines for downhole usage.

[0002] In view of the existence of the foregoing problems relating to usage of sodium thiocyanate in concentrated brines for downhole usage, an investigation has been made to see if a cause for such sodium thiocyanate decomposition might be found. Pursuant to this invention, a cause for such decomposition has now been discovered, and an effective solution to the problem has been found.

THE INVENTION

[0003] It has been discovered that even trace amounts of methanol plays a role in decomposing sodium thiocyanate, a representative inorganic thiocyanate corrosion inhibitor, whereby methyl mercaptan, dimethyl sulfide, and dimethyl disulfide are produced. These substances are highly corrosive and will readily attack corrosion resistant alloys. On the other hand, it has been found that under the same conditions, ethanol does not cause formation of corrosive components that will attack corrosion resistant alloys.

[0004] Thus per this invention, in an oilfield brine solution in which an inorganic thiocyanate corrosion inhibitor such as sodium thiocyanate is used, the brine is improved by providing and/or using a brine in which there is an absence of a thiocyanate-decomposing amount of methanol.

[0005] Various methods and compositions constituting embodiments of this invention will be still further apparent from the ensuing description and appended claims.

[0006] Oilfield downhole operations in which concentrated aqueous brine solution can be used include drilling, completion, packer, and gravel packing. Such methods are well known to those of ordinary skill in the art, and are described in the literature. See for example *A Primer of Oilwell Drilling*, 5th Edition, Revised by Ron Baker, Austin, Texas, 1996; and *Completion and Workover Fluids*, Monograph, Volume 19 SPE, by Kenneth L. Bridges, Richardson, Texas, 2000. The disclosures of each of these reference works to the extent they relate to downhole operations in which a concentrated aqueous brine solution is or can be used are incorporated herein by reference.

[0007] One potential source of methanol is in the brine itself inasmuch as methanol can be used as component, often as a bromine scavenger, in the manufacture of concentrated aqueous brine solutions for use in downhole operations, or can be used in the manufacture of, or as a solvent for, additives for use in such brine solutions. See for example U.S. Pat. Nos. 4,514,374, 4,549,973; 4,753,740; 4,784,796; 4,784,797; and 5,230,879, the full disclosures of which are incorporated herein by reference. Such concentrated brine solutions can be aqueous solutions of such halide salts as calcium chloride, calcium bromide, zinc chloride, zinc bromide, sodium chloride, sodium bromide, potassium chloride, potassium bromide, or like water-soluble salts. Commercially-available brines of this type include a concentrated aqueous solution of sodium bromide, a concentrated aqueous solution of calcium bromide, and a concentrated aqueous solution of a mixture zinc and calcium bromides. In each such solution these specified metal bromides are in whatever dissolved, dissociated, ionized, complexed, and/or solvated form(s) in which they exist when in solution in an aqueous medium. Typically the sodium bromide solutions have contents corresponding to the range of about 38 to about 47 wt% of sodium bromide in whatever form(s) in which sodium bromide exists when in solution in an aqueous medium. Typically the calcium bromide solutions have contents corresponding to the range of about 48 to about 57 wt% of calcium bromide in whatever form(s) in which calcium bromide exists when in solution in an aqueous medium. Typically the mixed zinc bromide and calcium bromide solutions have contents corresponding to the range of about 53 to about 60 wt% of zinc bromide and corresponding to the range of about 17 to about 22 wt% of calcium bromide in whatever form(s) in which these two bromides exist when both are in solution in the same aqueous medium. In each case the balance to 100 wt% is water. These brines may be blended with one another in any proportions. Also these brines may be mixed with another halide salt whether such salt is in the solid state or as a brine solution to afford a mixture with the desired density for the operation in which the resultant mixed solution will be used. For example, a composite brine

with a density of 13.3 lbs/gal at 70°F (ca. 1.6 kgs/liter at 21°C) can be formulated using 0.4155 bbl of an 11.6 lbs/gal calcium chloride brine with 0.4826 bbl of a 14.2 lbs/gal calcium bromide brine and 77.9 lbs of 80% calcium chloride solid salt.

[0008] Pursuant to this invention, when employing a thiocyanate corrosion inhibitor in a concentrated brine solution for downhole usage, one should ensure that there is no thiocyanate-decomposing amount of methanol in the brine. Among analytical procedures that can be used are gas chromatography, mass spectroscopy, and nuclear magnetic resonance spectroscopy. The following NMR procedure is illustrative and recommended:

[0009] In general, deuterium oxide is added to a sample under test. The proton NMR spectrum for samples in water is obtained under water suppression conditions when necessary to observe very low levels of methanol. The methanol content is identified and the concentration estimated. The methanol impurity is quantitated using a weighed internal standard and the weight percent of methanol is calculated from the weights and integrals.

[0010] A high-field NMR instrument capable of low power water suppression is used. High proton NMR sensitivity is required and a 400 MHz or higher field instrument is preferred. The chemicals employed in the procedure are deuterium oxide, 99.9 isotope % deuterium (Cambridge Isotopes DLM-4 or equivalent), and dimethylsulfoxide, reagent grade.

[0011] In conducting the procedure, the sample is diluted 1:2 or 1:3 in D₂O. Proton NMR spectra of the brines are obtained with suppression of the water resonance, as needed. The observed frequency is set on the water resonance. The minimum presaturation power is used to effectively suppress the water peak. This is typically a gamma H₂ of <50Hz with a presaturation time of 2s. Some adjustment of the power, irradiation frequency and other parameters as necessary to maximize water suppression while minimizing attenuation of any nearby peaks is employed. Presaturation power levels of 0.05-0.25% of maximum power are typical. Peaks within the 3.8-5.8 ppm chemical shift window (water peak at δ 4.8 ppm) can be expected to lose some intensity under these conditions.

[0012] Quantitation of methanol is accomplished as follows. Accurately weigh 2-6 grams of sample with 0.01-0.02 grams of reagent grade dimethylsulfoxide. Dissolve the sample in deuterium oxide. Obtain the proton NMR spectrum with 64K real data points and recycle time of 20-30 s. Obtain the appropriate peak integrals for the methanol species (δ 3.3 ppm)

and for the DMSO standard. Positive identification can be made via spiking with the authentic compounds.

[0013] The calculations employed are as follows:

Wt% of methanol species = A

Area of species = B

Area of standard = C

Wt of standard = D

Wt of sample = E

Using dimethylsulfoxide for standard: $A = (82.15) (B \times D) / (C \times E)$

[0014] Report no more than two significant figures for the impurity concentrations.

[0015] For determination or estimation of solid metal halide salts see below.

[0016] Quantitation of known impurities is accomplished as follows. Accurately weigh 1-4 grams of sample with 0.01-0.02 grams of reagent grade dimethylsulfoxide. Dissolve the sample in deuterium oxide. Obtain the proton NMR spectrum with 64K real data points and recycle time of 20-30 s. Obtain the appropriate peak integrals for the methanol species ($\delta \sim 3.3$ ppm) and for the DMSO standard.

[0017] Preferably, the analytical procedure used is employed prior to addition of an inorganic thiocyanate corrosion inhibitor to the solution.

[0018] Typical inorganic thiocyanates that, as a result of this invention, can be more efficiently used in concentrated aqueous oilfield brine solutions and in downhole operations therewith include sodium thiocyanate, potassium thiocyanate, ammonium thiocyanate, or a combination of any two or more of these. Typically they will be used in amounts in the range of about 0.05 to about 1 wt%, and preferably in amounts of about 0.1 to about 0.2 wt% based on the total weight of the solution including additives. Other additives that can be used in the compositions of this invention include hydrate inhibitors, scale inhibitors, thickeners, viscosifiers, and/or biocides.

[0019] The following Examples are presented for the purpose of illustration. They are not intended to limit the generic scope of the invention to the only the subject matter described therein.

EXAMPLES

[0020] As a demonstration of the efficacy of this invention, an experimental program was conducted for measuring thiocyanate decomposition as effected by the copresence of alcoholic additives. In three high pressure bombs were placed the following components, respectively:

Bomb 1) Aqueous calcium bromide brine (53 wt%) and 0.2 wt% sodium thiocyanate.

Bomb 2) Aqueous calcium bromide brine (53 wt%), 0.2 wt% sodiumthiocyanate, and 0.1 wt% methanol.

Bomb 3) Aqueous calcium bromide brine (53 wt%), 0.2 wt% sodiumthiocyanate, and 0.1 wt% ethanol.

The sealed bombs were held at 175°C and atmospheric pressure for 10 days. Then GC-MS analyses were conducted on the contents of the respective head spaces of these bombs. The Table summarizes the results of these analyses.

TABLE

Bomb No.	GC-MS Results
1	No H ₂ S, mercaptan, sulfide or disulfide were found.
2	No H ₂ S, Found: MeSSMe 15.7%, Me ₂ S 65.1%, and MeSH 0.1%. The balance to 100% was air.
3	No H ₂ S, mercaptan, sulfide or disulfide were found.

[0021] Without desiring to be bound by theory, one may explain the above results by suggesting that methanol reacts with thiocyanate by a second order nucleophilic substitution to afford methyl thiocyanate which is subsequently hydrolyzed to afford methyl mercaptan. By simple oxidation, some of this is then converted to dimethyl sulfide. On the other hand, these results indicate that ethanol does not undergo these reactions, at least under the conditions used.

[0022] It can be seen from the above that not only has a cause been discovered for the downhole corrosion problem due to the decomposition of an inorganic thiocyanate caused by the copresence of methanol in a concentrated brine solution but additionally, approaches to

solving this problem have been found. One involves methods and compositions in which the presence of methanol is avoided. A second involves the equally surprising discovery that ethanol can be substituted for methanol wherever methanol is used. For example ethanol can be substituted for methanol (a) in the manufacture of a concentrated brine solution at a production facility, or (b) as a raw material or component in a production process for making an additive to be incorporated into the concentrated brine solution before it is used in a downhole operation, or (c) as a solvent or diluent in the formulation of a formulated additive to be incorporated into the concentrated brine solution before it is used in a downhole operation.

[0023] Components referred to herein by chemical name or formula, whether referred to in the singular or plural, are identified as they exist prior to coming into contact with another substance referred to by chemical name or chemical type (*e.g.*, another component or a solvent). Also, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense (*e.g.*, "comprises" or "is"), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure.

[0024] This invention is susceptible to considerable variation within the spirit and scope of the appended claims.